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Preparation of p-type Hydrogenated Nanocrystalline Cubic Silicon Carbide / n-type Crystalline Silicon Heterojunction Solar Cells by VHF-PECVD

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Abstract

Aluminum doped p-type hydrogenated nanocrystalline cubic silicon carbide (Al-doped p-nc-3C-SiC:H) thin films were successfully deposited by very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) on n-type c-Si (n-c-Si) without serious damage by inserting an a-$Si_{1-x}C_x$:H buffer layer at p-nc-3C-SiC:H/n-c-Si interface as a protective layer against atomic hydrogen etching and a passivation layer. As a result, an active area efficiency of 17.0 % has been achieved without texturing [V_{oc}=0.648 V, J_{sc}=35.9 mA/cm^2, FF=0.732].

Keywords: nanocrystalline cubic silicon carbide; window layer; Al-doped; p-layer; VHF-PECVD; atomic hydrogen; crystalline silicon heterojunction solar cell

Introduction

Crystalline silicon heterojunction solar cells are one of the strong candidates for realizing high efficiency over 25 %. P-type hydrogenated amorphous silicon (p-a-Si:H) is generally used as the window layer of high efficiency n-type crystalline silicon (c-Si) heterojunction solar cells [1]. However, the p-type window layer limits short circuit current density (J_{sc}) due to its high light absorption in the range of 400 – 600 nm. A new wide band gap material is required for further improvement of the conversion efficiency. Hydrogenated nanocrystalline cubic silicon carbide (nc-3C-SiC:H) with wider bandgap of 2.2 eV and

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lower light absorption can be deposited at a low substrate temperature of about 360 ^{o}C by very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) [2-4]. Although it was reported that p-type crystalline silicon (p-c-Si) heterojunction solar cells with high-quality n-type nc-3C-SiC:H emitter achieved high efficiency of 17.9 % [5], the application of p-type nc-3C-SiC:H (p-nc-3C-SiC:H) emitter is expected to obtain higher open circuit voltage (V_{oc}) and conversion efficiency due to higher bulk lifetime of n-type c-Si than that of p-type c-Si.

In spite of very little study of p-nc-3C-SiC:H [6,7], we have successfully deposited high quality p-nc-3C-SiC:H thin films on glass substrates by VHF-PECVD under the condition of higher H_2 dilution ratio than n-type 3C-SiC:H [8]. However, since large amount of atomic hydrogen is required to prepare p-nc-3C-SiC:H, the damage to the surface of the n-c-Si by atomic hydrogen etching is possible. To prevent the etching effects, it is effective to insert the buffer layer, which is a passivation layer and protective layer against atomic hydrogen etching of the crystalline silicon surface. In this study, we investigated the effects of an amorphous silicon carbide (a-$Si_{1-x}C_x$:H) buffer against atomic hydrogen etching during the deposition of p-nc-3C-SiC:H on the performance of n-type c-Si heterojunction solar cells with the p-nc-3C-SiC:H window layer.

Experimental

P-nc-3C-SiC:H films were deposited by VHF-PECVD using a mixture of monomethylsilane (MMS), hydrogen (H_2) and dimethylaluminum hydride (DMAH) at a low substrate temperature. Deposition conditions of p-nc-3C-SiC:H films are shown in Table I.

A-$Si_{1-x}C_x$:H films were also deposited by VHF-PECVD using a mixture of silane (SiH_4), MMS and H_2. The flow rates of MMS and SiH_4 were kept constant at 2.5 sccm and 5 sccm, respectively. H_2 flow rate was changed in the range of 50 – 250 sccm. The substrate temperature, deposition pressure and interelectrode distance were kept constant at 180 ^{o}C, 50 Pa and 3 cm, respectively. The structure of a-$Si_{1-x}C_x$:H (2~25 nm)/n-c-Si (CZ, 1~10 Ωcm, 550 um)/a-$Si_{1-x}C_x$:H (50 nm) was fabricated for measuring the effective lifetime by microwave photoconductive delay (μ-PCD). In order to determine surface recombination velocity, the following equation is used,

$$\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}} = \frac{2S}{W} \quad (1)$$

where τ_{eff}, τ_{bulk}, S and W are effective lifetime, bulk lifetime, surface recombination velocity and bulk thickness, respectively. Considering the very high lifetime in n-type silicon bulk with low career concentration, the bulk lifetime can be ignored. Structural properties of the a-SiC:H films were characterized by Fourier transform infrared absorption (FTIR). Bonded hydrogen concentration of the films was calculated from the integrated peak intensity of Si-H_n stretching mode around 2000-2100 cm^{-1} using the proportional coefficient of 1.4×10^{20} cm^{-2} [9, 10].

N-c-Si heterojunction solar cells with the structure of Al/Ag/ITO/p-nc-3C-SiC:H/a-$Si_{1-x}C_x$:H/n-c-Si/n-a-Si:H/Al were also fabricated. To confirm the effects of atomic hydrogen etching, the thickness of an

Table I. Deposition conditions of p-nc-3C-SiC:H window layers

Plasma power density	2.23 W/cm^2	H_2 flow rate	500 sccm
Substrate temperature	390 ^{o}C	MMS flow rate	0.156 sccm
Interelectrode distance	4 cm	DMAH flow rate	0.131 sccm
Deposition pressure	800 Pa	H_2/MMS	3.2×10^3
Film thickness	40 nm		

a-$Si_{1-x}C_x$:H buffer layer, which is a passivation layer and protective layer against atomic hydrogen etching, is changed from 0 to 9 nm in this experiment.

Results and Discussion

The H_2/MMS flow rate ratio and dark conductivity of the p-nc-3C-SiC:H 26 nm-thick film were 8.5×10^3 and 6.8×10^{-4} S/cm, respectively. This electrical property is enough for the film to be applied to p-type window layer. We have already fabricated the heterojunction diode with the structure of Al/p-nc-3C-SiC:H/n-c-Si/n-a-Si:H/Al and have found that the diode was rectified [8]. Although this result revealed that Al-doped nc-3C-SiC:H is p-type, the interface properties have not been investigated enough yet. Therefore, we focused on the effects of p-nc-3C-SiC:H deposition condition for p/n interface. Fig. 1. shows cross-sectional TEM image of p-nc-3C-SiC:H thin film directly deposited on a polished n-c-Si wafer. Unintentionally, the Si surface was etched by large amount of atomic hydrogen which was generated under the deposition condition of p-nc-3C-SiC:H due to very high hydrogen dilution ratio, power density and pressure. It was cleared that this etching caused serious damage to Si surface. This led to increase interface defect density and decrease V_{oc}. N-c-Si heterojunction solar cells with the structure of Al/Ag/ITO/p-nc-3C-SiC:H/n-c-Si/n-a-Si:H/Al were also fabricated. The value of V_{oc} is less than half of conventional c-Si heterojunction solar cells, 302 mV. In order to obtain higher V_{oc}, further improvement of p/n interface properties is required.

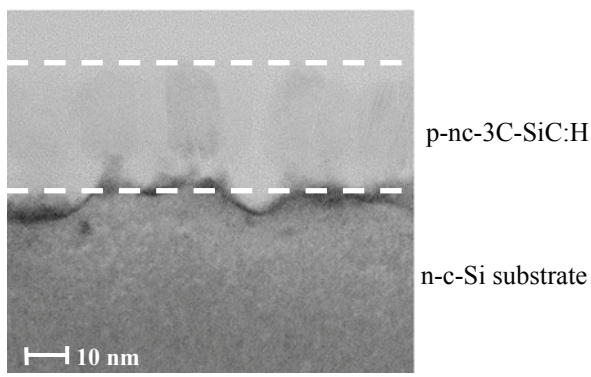
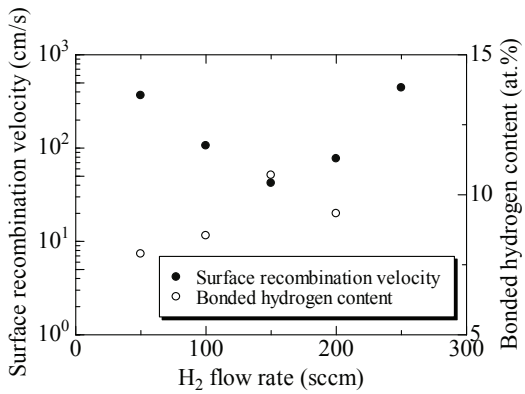


Fig. 1. TEM image of p-nc-3C-SiC:H thin film on flat n-c-Si without any buffer layer

To control p/n interface, we tried to insert an a-$Si_{1-x}C_x$:H buffer layer. A-$Si_{1-x}C_x$:H is more suitable than a-Si:H for a protective layer with high passivation effect and durability for atomic hydrogen etching because Si-C bonding is stronger than Si-Si bonding [11, 12]. Fig. 2. shows the dependence of H_2 flow rate on surface recombination velocity and bonded hydrogen content in a-$Si_{1-x}C_x$:H films measured by FTIR. The surface recombination velocity is decreased by increasing H_2 flow rate up to 150 sccm. On the other hand, the more H_2 flow rate caused high surface recombination velocity. The surface recombination velocity was in inverse proportion to the amount of bonded hydrogen content. From these result, the passivation effect of a-$Si_{1-x}C_x$:H buffer layer was optimized at H_2 = 150 sccm.

To obtain high passivation effects, thicker buffer layer is better, however, it causes the deterioration of solar cell performances. Therefore, the thickness of the buffer layer has to be optimized. Dependence of a-$Si_{1-x}C_x$:H layer thickness on surface recombination velocity was shown in Fig. 3. In the range of 2-10 nm, the surface recombination velocity was decreased by increasing a-$Si_{1-x}C_x$:H thickness. This indicated

that very thin defective layer covered polished Si surface [13]. On the other hand, the surface recombination velocity was saturated over 10 nm.



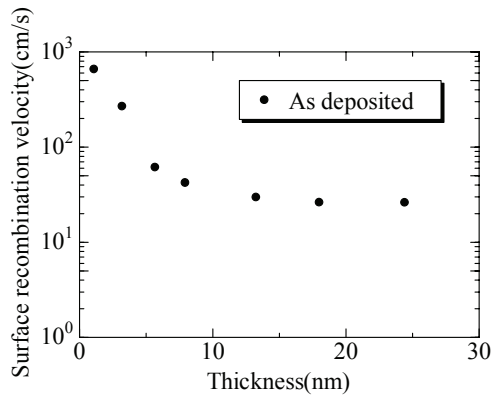


Fig. 2. Dependence of H_2 flow rate on surface recombination velocity and bonded hydrogen content in a-$Si_{1-x}C_x$:H films (left figure).

Fig. 3. Dependence of a-$Si_{1-x}C_x$:H layer thickness on surface recombination velocity (right figure).

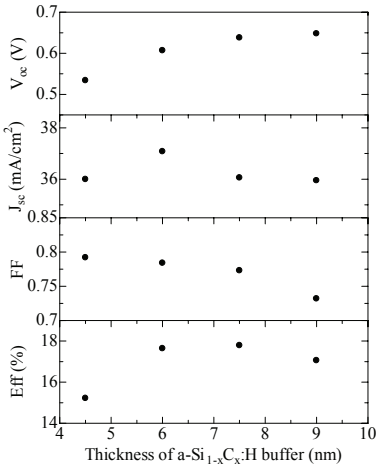
We also fabricated heterojunction solar cells with the structure of Al/Ag/ITO/p-nc-3C-SiC:H/a-$Si_{1-x}C_x$:H/n-c-Si/Al. The optimized a-$Si_{1-x}C_x$:H buffer layer was inserted between p-nc-3C-SiC:H and n-c-Si. Moreover, to reduce the exposure time of a c-Si surface to atomic hydrogen, the deposition rate of p-nc-3C-SiC:H was increased by controlling the deposition pressure. Fig. 4 shows the effects of thickness of a-$Si_{1-x}C_x$:H buffer layer on solar cell parameters. Increase of thickness of buffer layer led to decreasing FF due to increasing series resistance. V_{oc} was increased by increasing i-layer thickness. This result corresponds to effective lifetime measurement by μ-PCD. High J_{sc} indicates that p-type window layer has low light absorption in spite of the p-layer thickness of 40 nm. As a result, an active area efficiency of 17.0 % has been achieved without texturing [V_{oc}=0.648 V, J_{sc}=35.9 mA/cm^2, FF=0.732].

The structural properties were also investigated to confirm a-$Si_{1-x}C_x$:H as a protective layer. The cross-sectional TEM image of p-nc-3C-SiC:H/n-c-Si heterojunction solar cell is shown in Fig. 5. Compared with Fig. 1, silicon surface was completely covered by an a-$Si_{1-x}C_x$:H buffer and had no serious damage by atomic hydrogen etching. That is why p-nc-3C-SiC:H/n-c-Si heterojunction solar cell achieved higher V_{oc}. The etching rate of a-$Si_{1-x}C_x$:H buffer by H_2 plasma is very high, about 0.4 nm/s. Therefore, the a-$Si_{1-x}C_x$:H buffer layer the a-$Si_{1-x}C_x$:H buffer layer became victim to the etching by atomic hydrogen and protected the surface of c-Si from the etching while p-nc-3C-SiC:H was deposited. From the ring spacing of the electron diffraction pattern, the lattice constant of this nanocrystalline was calculated and found to be 0.433 nm, which was same as that of 3C-SiC. Another crystalline phase was also found at a-$Si_{1-x}C_x$:H/n-c-Si interface. According to the electron diffraction pattern at the interface, the epitaxial crystalline phase was found to be silicon. This indicated that epitaxial silicon was grown by high H_2 dilution during the a-$Si_{1-x}C_x$:H deposition. The darker contrast of epitaxial Si than that of polished n-c-Si wafer is due to its random orientations. As a result, a-$Si_{1-x}C_x$:H worked as a protective layer with high passivation effect and durability for atomic hydrogen etching.

Conclusion

We investigated the effects of atomic hydrogen on the interface and solar cell properties. Since a very large amount of atomic hydrogen is required to prepare p-nc-3C-SiC:H, the Si surface is unintentionally etched by atomic hydrogen before the deposition, and then, the V_{oc} of a c-Si solar cell decreases. In order

to solve this problem, we tried to insert hydrogenated amorphous silicon carbide as a protective layer with high passivation effect and durability for atomic hydrogen etching. Moreover, to reduce the exposure time



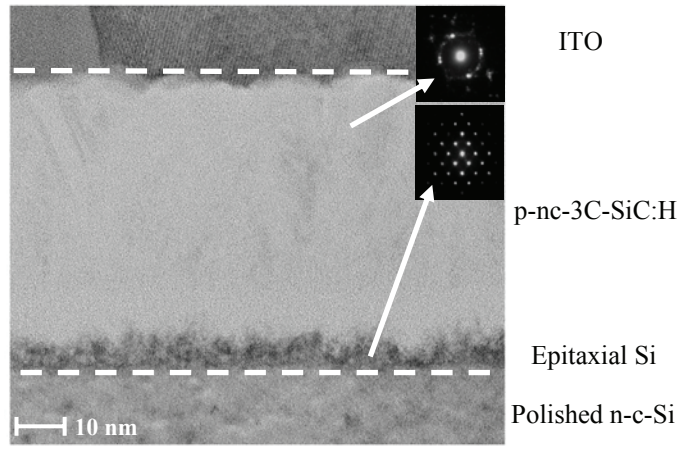


Fig. 4. The effects of thickness of a-Si$_{1-x}$C$_x$:H buffer layer on solar cell parameters (left figure)
Fig. 5. TEM image of p-nc-3C-SiC:H/n-c-Si heterojunction solar cell (right figure)

of a c-Si surface to atomic hydrogen, the deposition rate was increased by increasing the deposition pressure. As a result, the V_{oc} of a c-Si heterojunction solar cell was improved from 302 mV to 648 mV. An active area efficiency of 17.0 % has been achieved without texturing [V_{oc}=0.648 V, J_{sc}=35.9 mA/cm^2, FF=0.732].

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